Novel Approaches for Speciation of Platinum and Vanadium in Mobile Source Emissions

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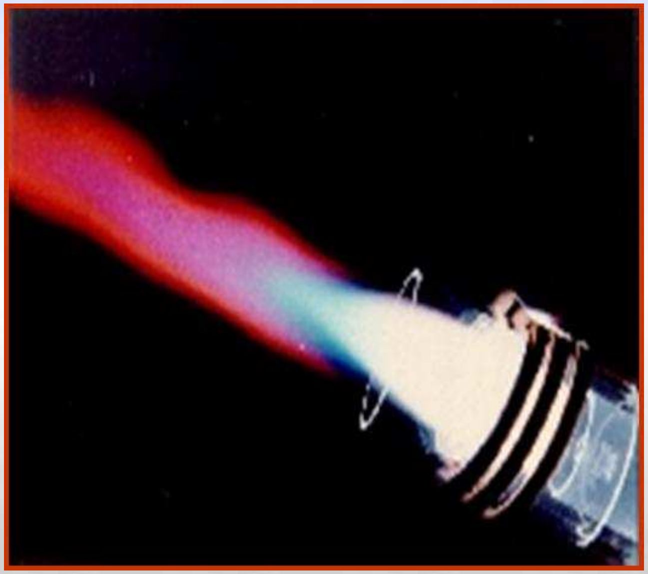


AAAR 27TH Annual Conference

Motivation

- Controlling emissions from mobile sources are critical for continued reduction in health impacts of air pollution, and for addressing regional and global climate impacts.
- Most current and proposed emission control strategies for diesel and gasoline engines employ metal catalysts to reduce tailpipe emissions of regulated species.
  - *Gasoline Three-Way-Catalysts (Pt, Pd, Rh)*
  - *Diesel Fuel Based Catalysts (Pt-FBC)*
  - *Diesel Particulate Filters (Pt-Catalyzed)*
  - *Diesel Selective Catalytic Reactors (V-SCR)*
- The use of these metals raises concerns about potential environmental contamination and the health implications of widespread trace metal dissemination.

MOTIVATION

- **The toxicological responses of many metals (e.g. Cr, Cu, Mn, Pt, V) are determined by the specific chemical & physical speciation in the emissions.**
  - **Platinum: soluble, oxidized, halogenated (e.g. chloroplatinic acids) species are 500 fold more toxic than metallic species.**
  - **Vanadium: pentoxide V(V) species exhibits much greater toxicity than the lower oxidation state species.**

- **Problem and Challenge:**
  - ☹ **Extant modern methodologies provide little relevant speciation information.**
  - ☹ **Traditional techniques that are speciation capable lack the required sensitivity, particularly in the context of lower emissions from vehicles equipped with modern control devices.**

Engine Exhaust PM Characterization

- **Elemental & Isotopic Characterization**
  - ***Magnetic sector (high resolution) ICP-MS***
    - ***Sensitivity and Interference Isolation***
- **Chemical & Physical Speciation of PM**
  - Solubility
  - Oxidation State
    - **Soluble Species:**
      - *Long-path (100 cm) Spectrophotometry with Characteristic Ligand e.g. Fe(II)/Fe(III), Mn(II)/Mn(>III), Cr(III)/Cr(VI)*
      - ***Immobilized Ligand – Selective Extraction and Elution***
    - **Direct Solids:**
      - ***Synchrotron X-ray Absorption Spectroscopy***
  - Colloid Charge: *Ion Chromatography (DEAE, SAX micro-columns) → ICP-MS*
  - Colloid Size: *Ultrafiltration (10, 100 kDa) → ICP-MS*

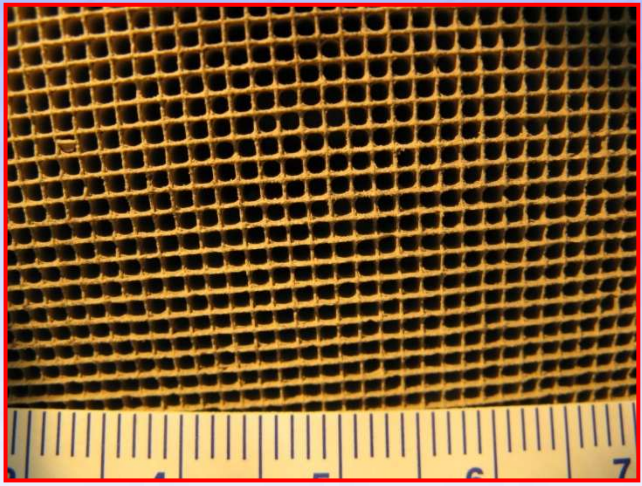
Complementary Total and Extractable Methods

Speciation Background

- **Platinum**
  - Oxidation States (0, II, IV). Group 8 transition metal.
  - Higher oxidation states may be more soluble.
  - Chloroplatinic/um salts (H, NH_4, K, Na) are very soluble.
- **Vanadium**
  - [Ar] $3d^3$ $4s^2$. Forms oxyanions. Amphoteric. Redox Active.
  - Oxidation States: (0,II,III,IV,V).
  - Higher oxidation states more soluble in water due to hydrolysis.
  - V(V): (high pH) VO_4^{3-}, HVO_4^{2-}, $H_2VO_4^-$, H_3VO_4, VO_2^+ (low pH).
  - V(IV): cationic (VO^{2+})

Platinum: Sources and Receptors Under Study

- Three-Way-Catalysts
- Size-Resolved PM from Engines burning Platinum-Amended Diesel Fuel
- PM from Platinum-Catalyzed DPF
- Roadside Dust / Soils

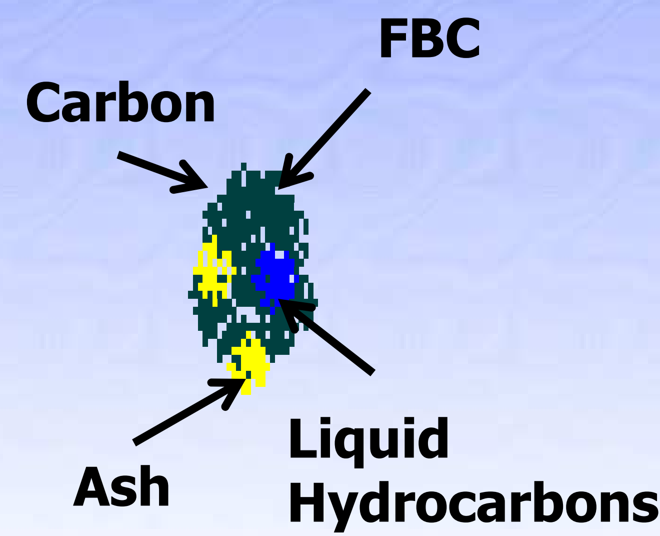


25 mm PCIS Substrate

Gasoline Engine Catalytic Converter

What is a Fuel-Borne Catalyst?

- **Catalyst dosed directly into diesel fuel**
  - Pt / Ce fuel-soluble bimetallic catalyst
  - delivered *in situ*
- **Active in high temperature combustion zone**
  - higher efficiency of fuel HC combustion
- **FBC intimate contact with PM**
  - more complete combustion of solid C, HC
  - uniformly distributed across PM size range
  - no increase in ultra-fines
- **Delivers Catalyst to DOC / DPF**
  - fresh catalyst surface replenishment
  - same active forms
  - permits lower lifetime use of Pt



Platinum: Analytical Speciation of Engine PM

- **Solid Phase**
  - Total: microwave/acid digestion – HR-ICP-MS
  - **Oxidation State: Synchrotron XAS**
- **Extractable Species**
  - Primarily oxidized and halogenated species
  - Total “soluble” - HR-ICP-MS
    - ***Water***
    - ***Methanol***
    - ***DCM***
  - Ultra-filtration: colloidal versus “dissolved”
  - Ion Chromatography: anionic versus cationic
  - HPLC-IC-HR-ICP-MS: specific chemical species
- **Particle Size Distribution**
  - Sioutas PCIS (5 size-cuts)

Analytical Challenge: <1 ng extractable platinum (10-30 pg in specific fractions).

Speciated Water Soluble Platinum in Diesel PM

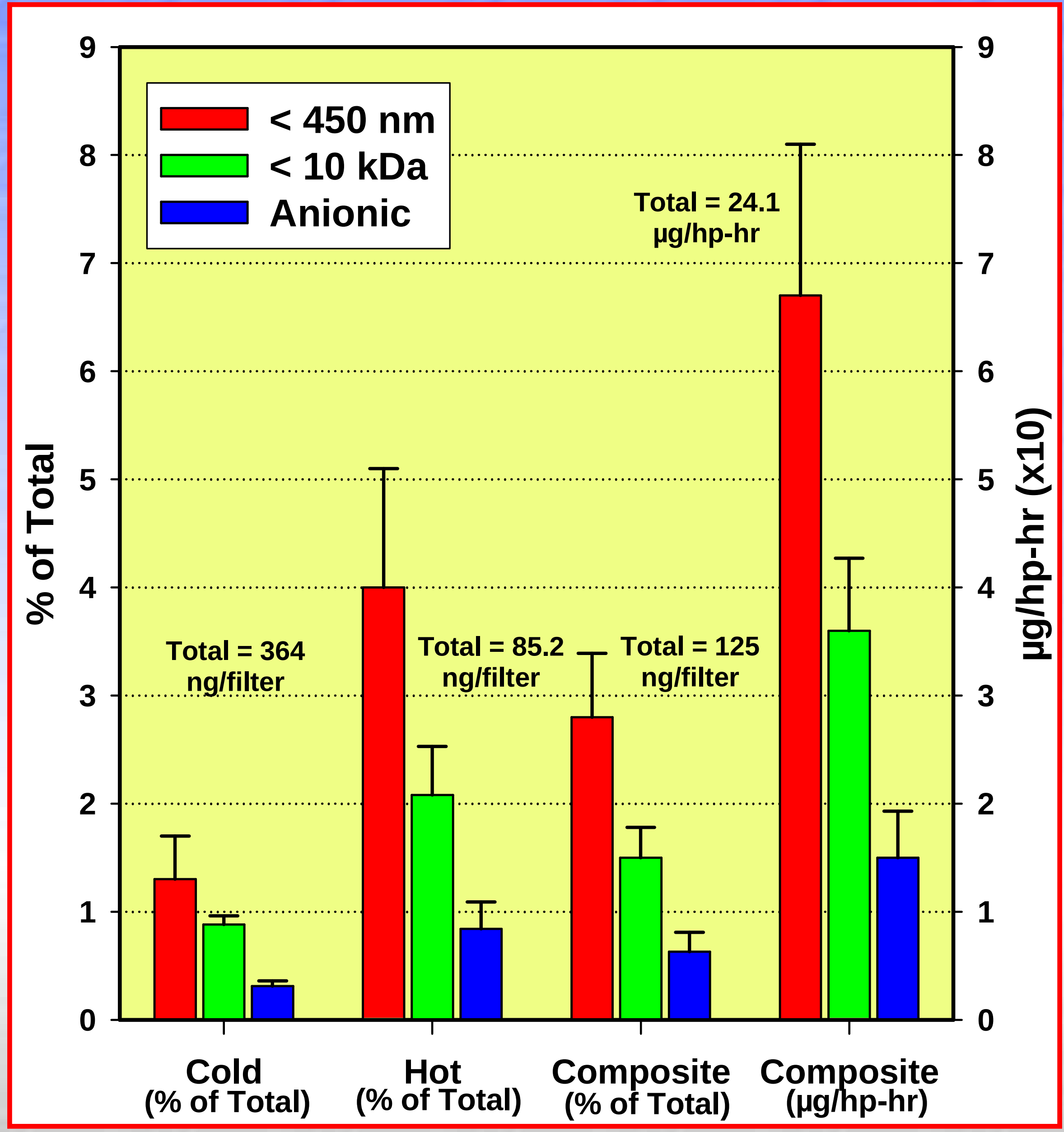
FTP Cycle Means

Extractable fraction = < 3%.

Large colloidal fraction (44% of extractable species).

Dissolved (<10 kDa) species exhibit significant anionic character on DEAE (42%).

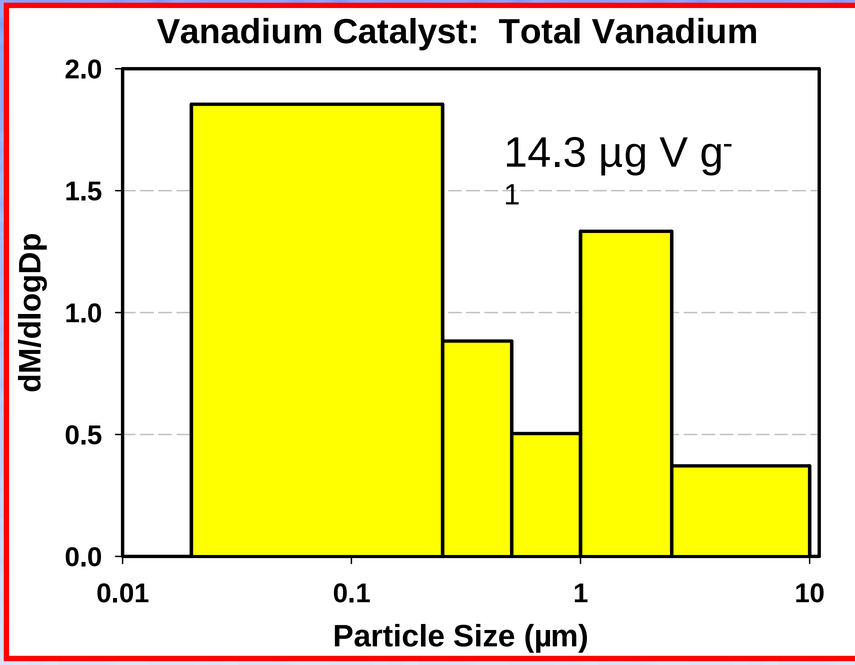
Shafer, M.M., J.J. Schauer, W. Copan, J. Peter-Hoblyn, B. Sprague, and J. Valentine. 2007. Investigation of platinum and cerium from use of a fuel-based catalyst. *SAE 2006 Transactions Journal of Fuels and Lubricants –* 2006-1-1517:491-503.

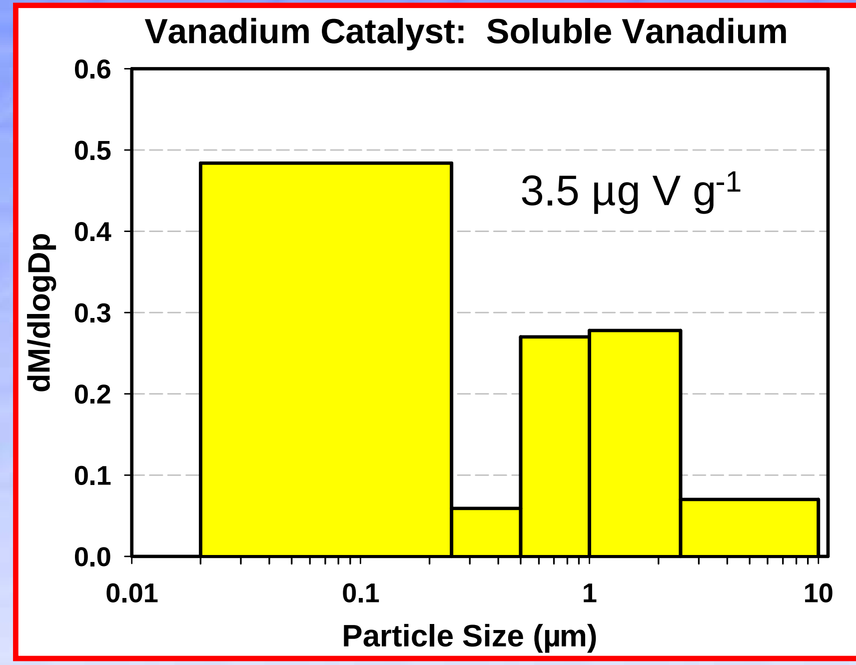


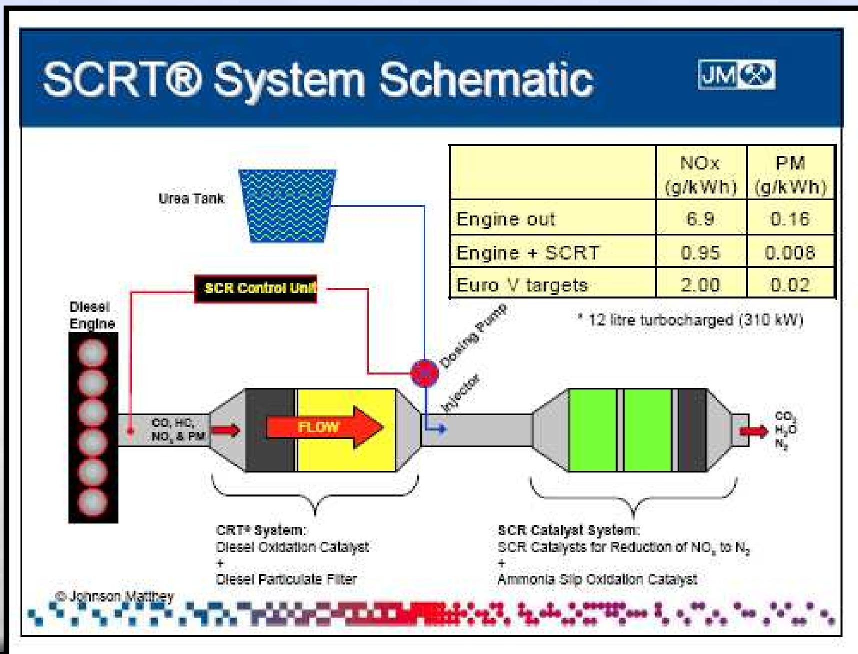
Vanadium: Analytical Speciation of Engine PM and Urban Aerosol

- Solid Phase
  - Total: microwave/acid digestion – HR-ICP-MS
  - **Oxidation State: Synchrotron XAS**
- Extractable Species
  - Primarily V(V) and V(IV)
  - Total water and acetate soluble: HR-ICP-MS
  - **[V(II), V(III)] V(IV), V(V) : Immobilized ligand speciation**
- Particle Size Distribution
  - Sioutas PCIS (5 size-cuts)

Significant Analytical Challenge: 0.2-2 ng total vanadium from Dyno Trials for speciation studies.

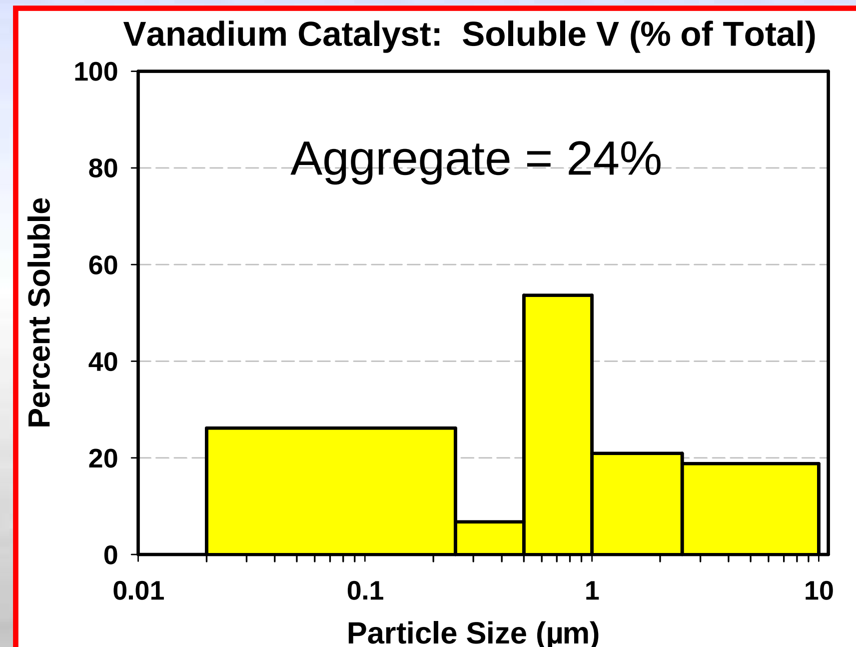






	NOx (g/kWh)	PM (g/kWh)
Engine out	6.9	0.16
Engine + SCRT	0.95	0.008
Euro V targets	2.00	0.02

* 12 litre turbocharged (310 kW)

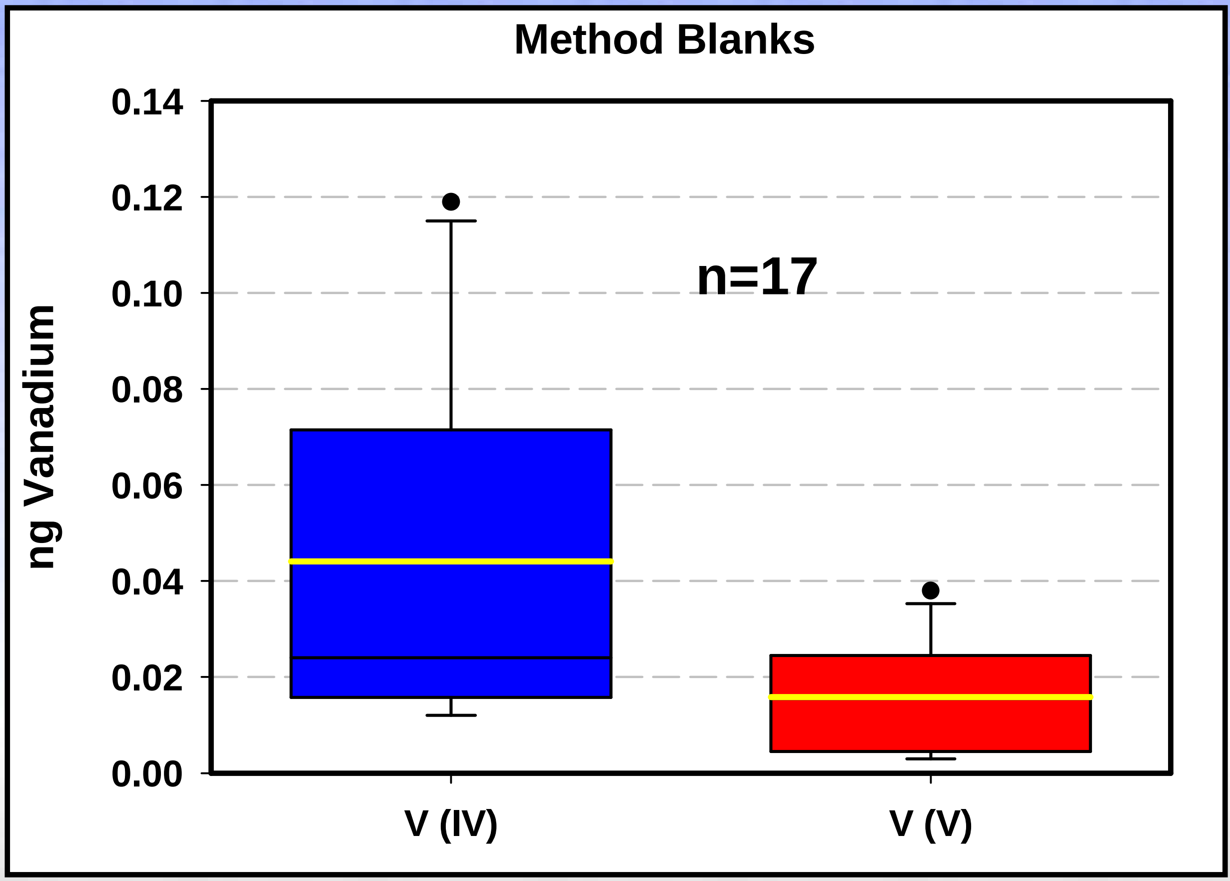


Vanadium Oxidation State Speciation with Chelex

Chelex: cation exchanger at higher pH, anion exchanger at lower pH. In pH range of 4 to 7.4 both cations and anions are adsorbed.

- **Preparation & Extraction**
  - Micro-columns of Chelex (immobilized iminodiacetate)
    - 0.2 g of perchloric acid cleaned and acetate buffered (pH=4.5) resin
  - Samples extracted in 2 mM sodium acetate buffer
    - 1.5 mL nitrogen purged buffer in purged cryo-vial
    - 60 minutes with defined agitation (under nitrogen canopy)
- **Separation – Speciation**
  - 1.0 mL of sample loaded onto column
  - Process through column at 1.0 mL per minute – collect fraction
  - Elute column with 4 x 1 mL of 0.1 M ammonium hydroxide – collect fraction = **V(V).**
  - Elute column with 2 x 1 mL of 0.2 M perchloric acid – collect fraction = **V(IV)**
- **Vanadium Quantification**
  - Magnetic Sector ICP-MS in medium resolution with on-line standard addition
  - 10,000 cps/ppb V. Background = ~2 cps (0.2 ng L^{-1}). 1-5% RSD.

Vanadium Oxidation State Speciation with Chelex

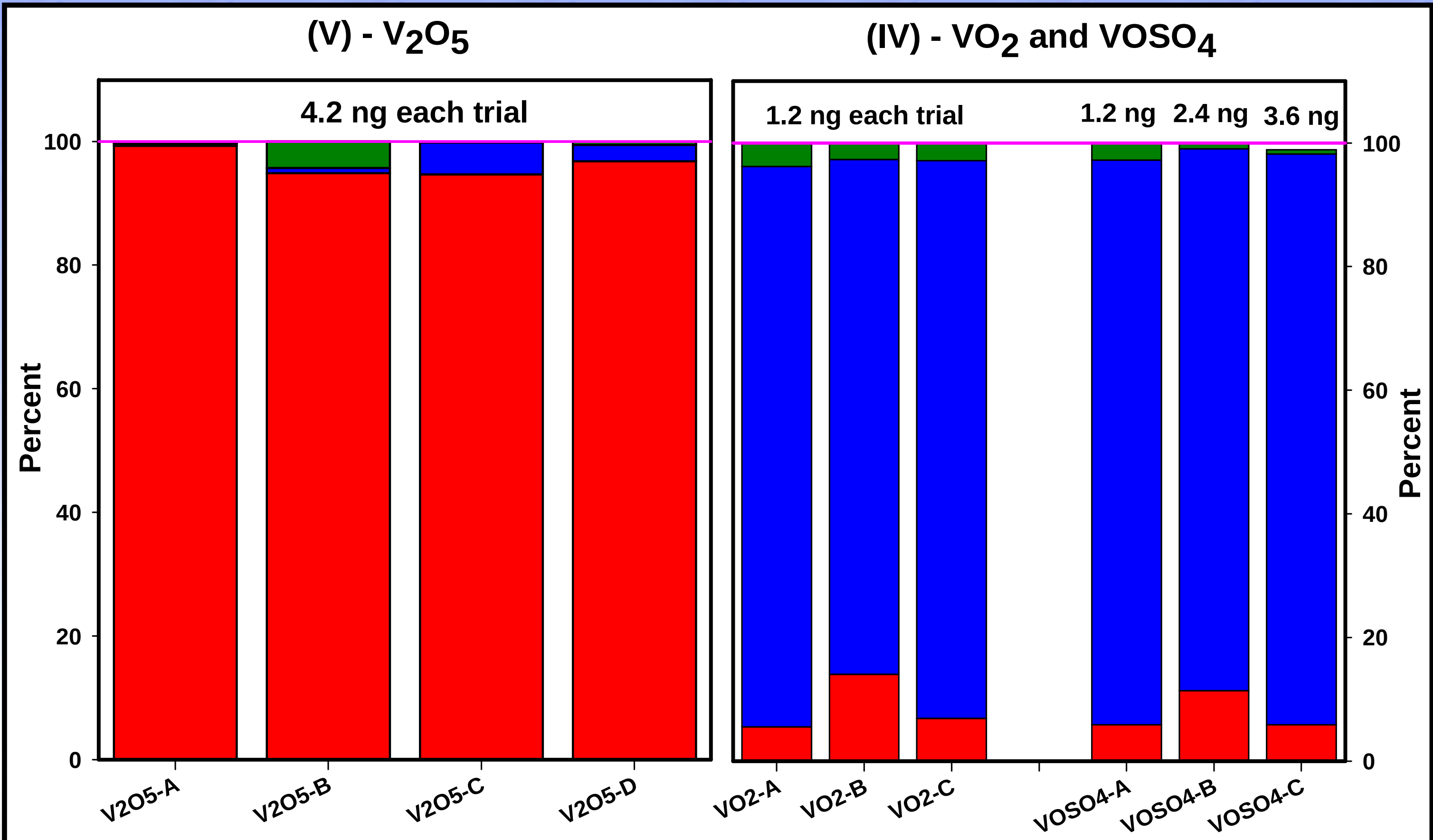


0.044 ± 0.037 ng **0.016 ± 0.011 ng**

(IV) DL=0.11 ng (0.44 ppm)

(V) DL=0.03 ng (0.14 ppm)

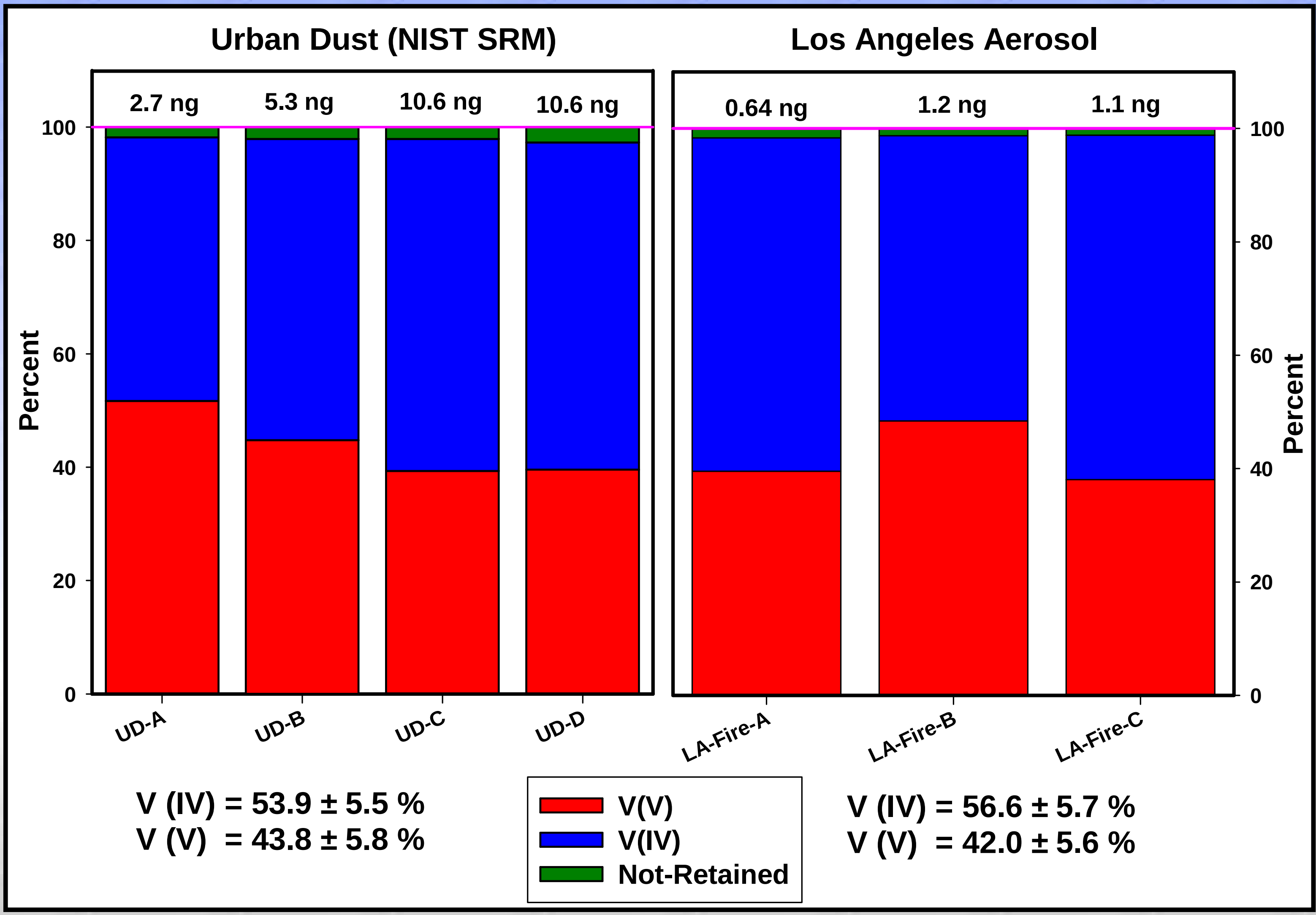
Vanadium Speciation – Defined Standards



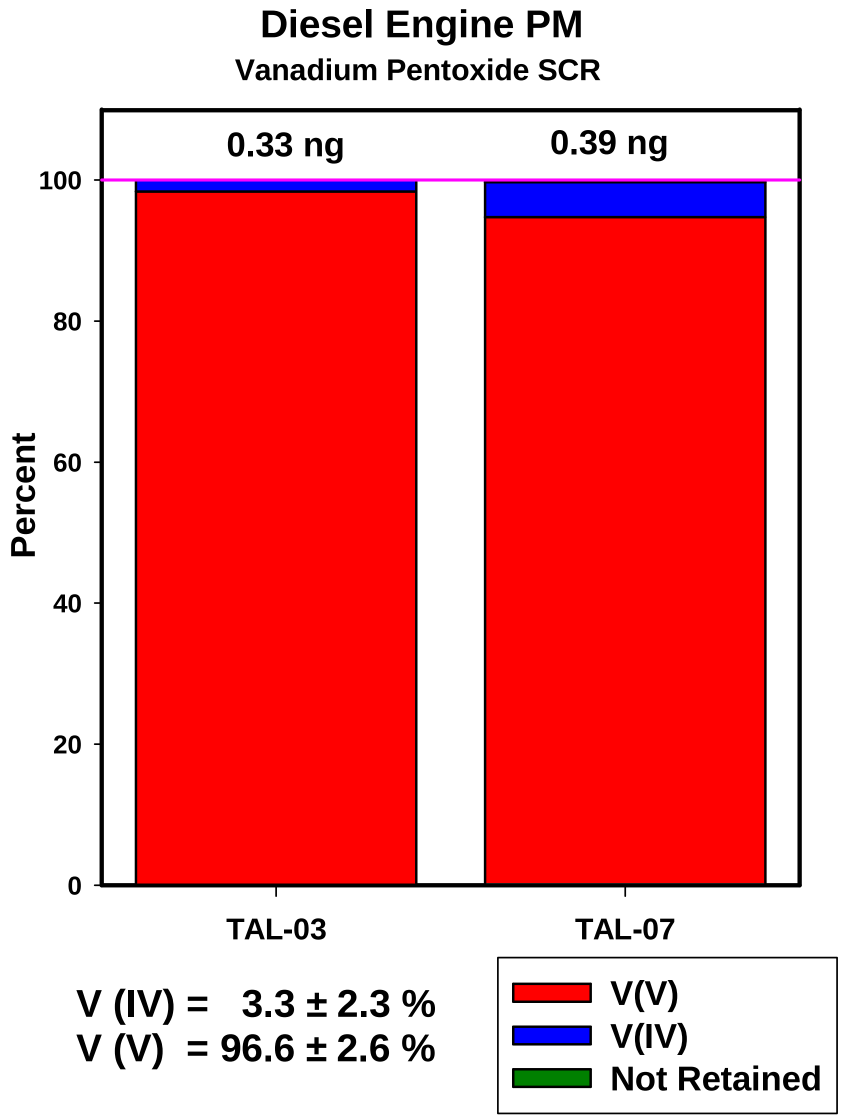
V (V) = 96.4 ± 2.2 %

V (IV) = 89.3 ± 3.3 %

Vanadium Speciation – Environmental Matrices



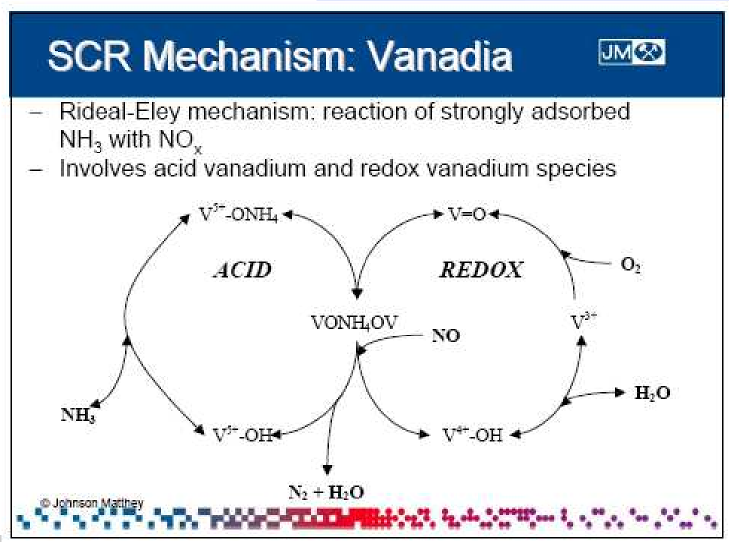
Vanadium Speciation – Engine Exhaust PM



V (IV) = 3.3 ± 2.3 %
V (V) = 96.6 ± 2.6 %

ADVANCES

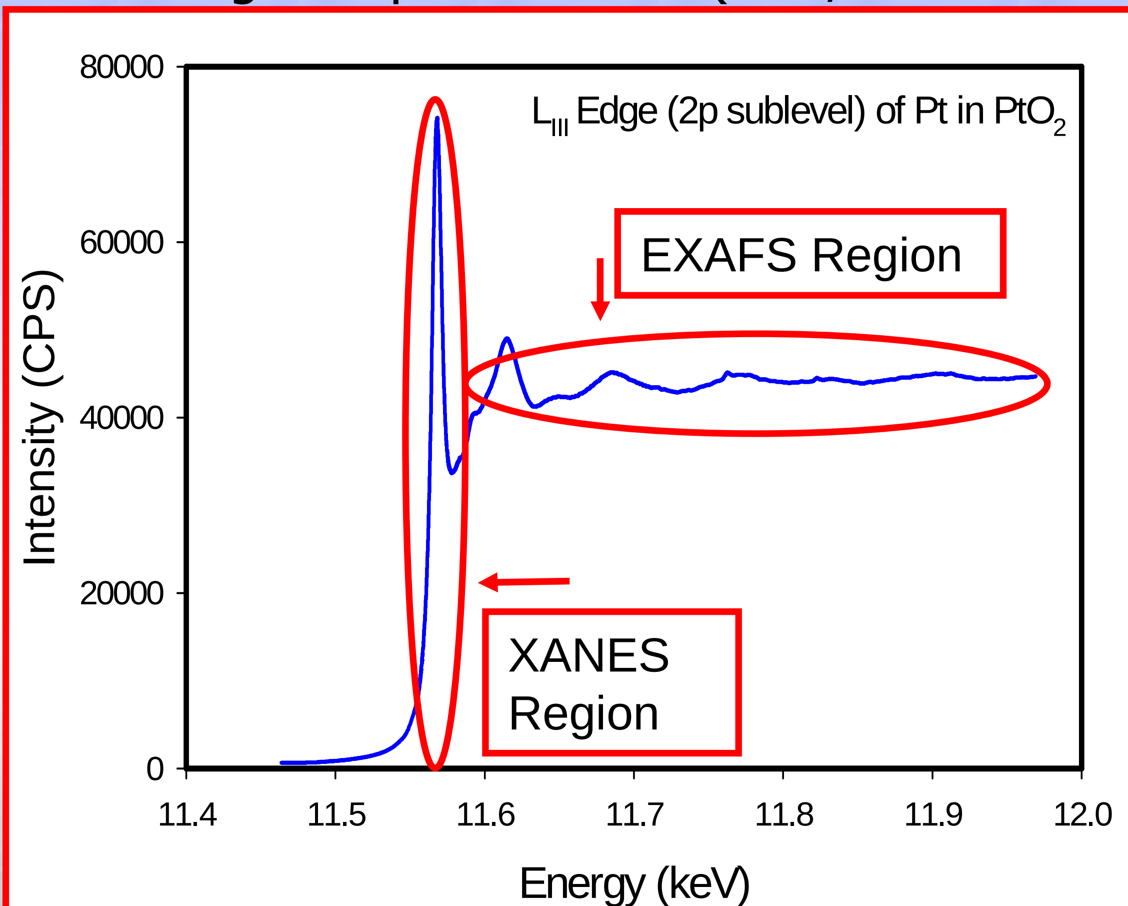
1. Micro-scale
2. DLs improved by 10-50x
3. Coupling to HR-ICP-MS

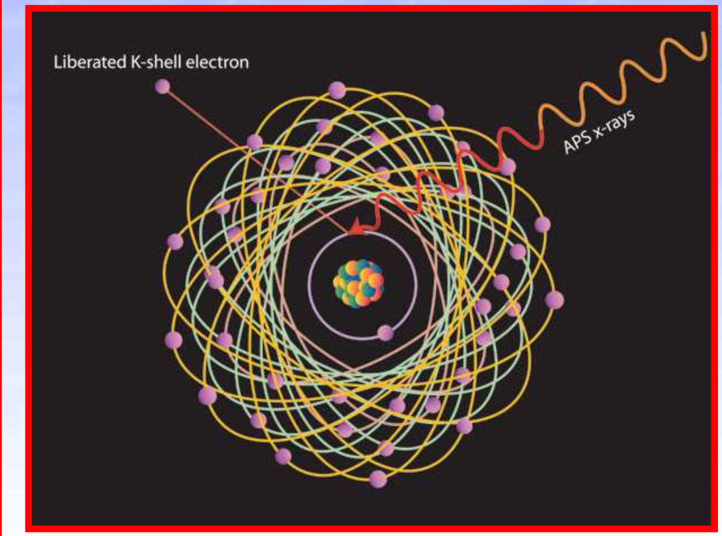


Wang D. and S. Sanudo-Wilhelmy 2008 Marine Chemistry.

Synchrotron X-Ray Absorption Spectroscopy

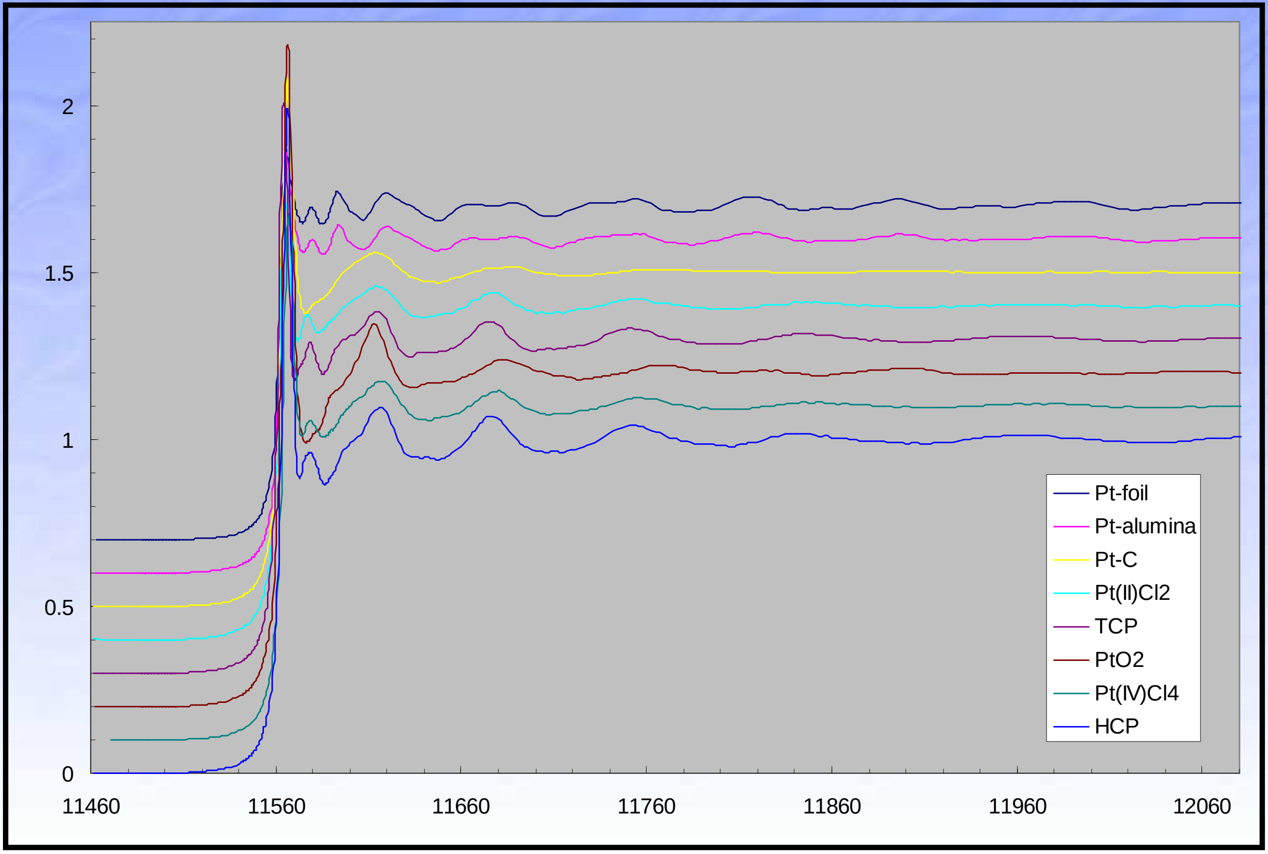
- Direct Solids Analysis – complementary to solution phase tools.
- XANES – (oxidation state) and/or EXAFS – (nearest neighbor chemical bonding environment). XRD – (characteristic diffraction)
- Range of spatial scales (with/without micro-focused beamline).





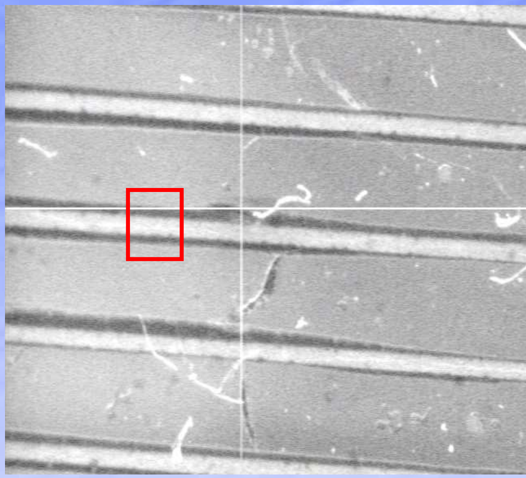
Majestic, B.J., J.J. Schauer, M.M. Shafer. 2007. Application of Synchrotron Radiation for Measurement of Iron Red-Ox Speciation in Atmospherically Processed Aerosols. Atmospheric Chemistry and Physics 7:2475-2487.

EXAFS Spectra of Platinum Reference Materials

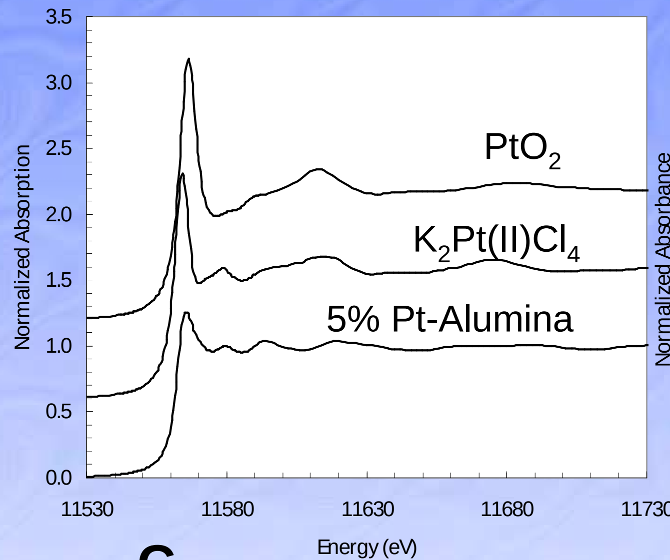


LBL-Advanced Light Source

Pt-foil = platinum foil; Pt-alumina = 5% platinum on alumina; Pt-C = 5% platinum on graphite; Pt(II)Cl2 = platinum(II) chloride; TCP = potassium platinum(II) tetrachloroplatinate; PtO2 = platinum(IV) oxide; Pt(IV)Cl4 = platinum(IV) chloride; HCP = potassium platinum(IV) hexachloroplatinate



A



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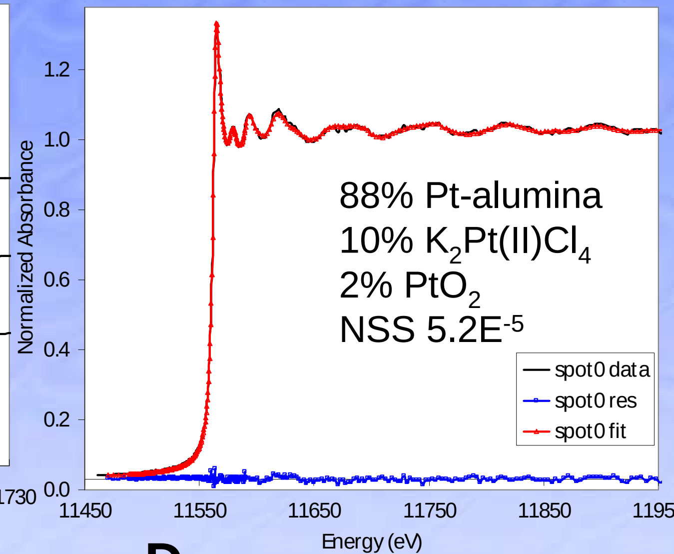

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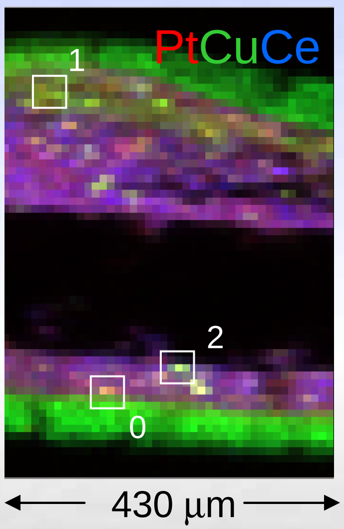


B

Pt speciation was studied in a 4 year old 3-way automobile catalyst. A 30 µm thick, quartz slide mounted, longitudinal section of the center of the catalyst was prepared.

(A) Light microscope image; outlined area was examined with XRF mapping.

(B) Red (Pt) – green (Cu) – blue (Ce) XRF-derived tricolor map. Pt L3-edge extended-XANES spectra were collected at spots 0-2.

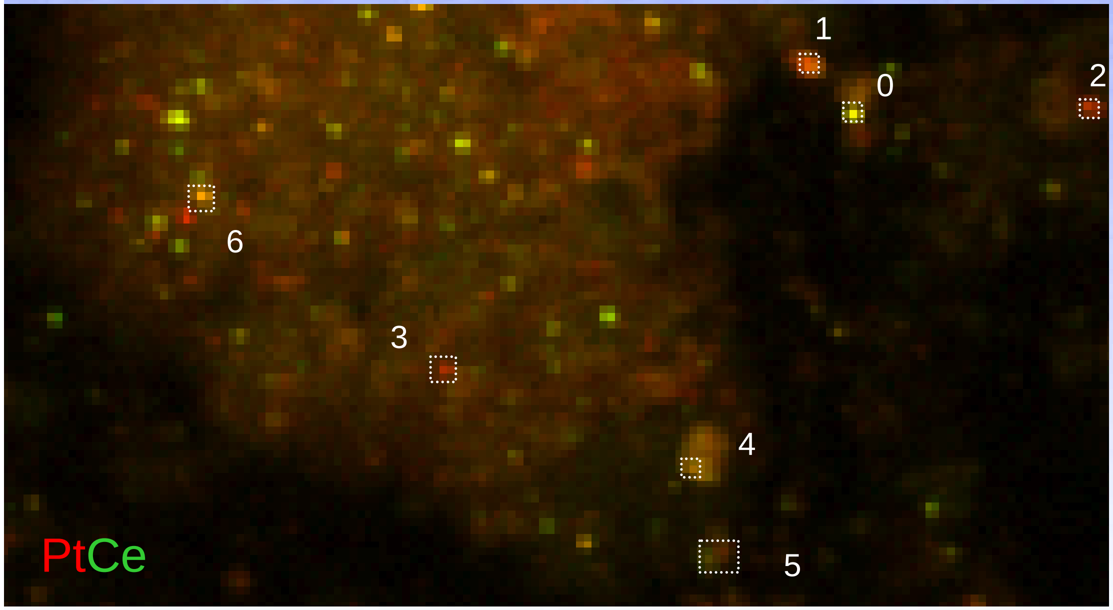
(C) The e-XANES spectra (11,466-12,077 eV) were fit with reference spectra - Pt foil, 5% Pt in alumina matrix, 5 % Pt in carbon matrix, $Pt(II)Cl_2$, $Pt(IV)Cl_4$, PtO_2, $K_2Pt(IV)Cl_6 \cdot H_20$, and $K_2Pt(II)Cl_4$ – by linear least squares method

(D) Select reference spectra and an example fit shown in C and D).

Modeled fraction of oxidized Pt is significant.

XRF Map, and Extended-XANES Fitting Results, of Diesel Exhaust Particulates Trapped on a Diesel Particulate Filter (engine running a Pt-FBC)

X-ray Fluorescence Map



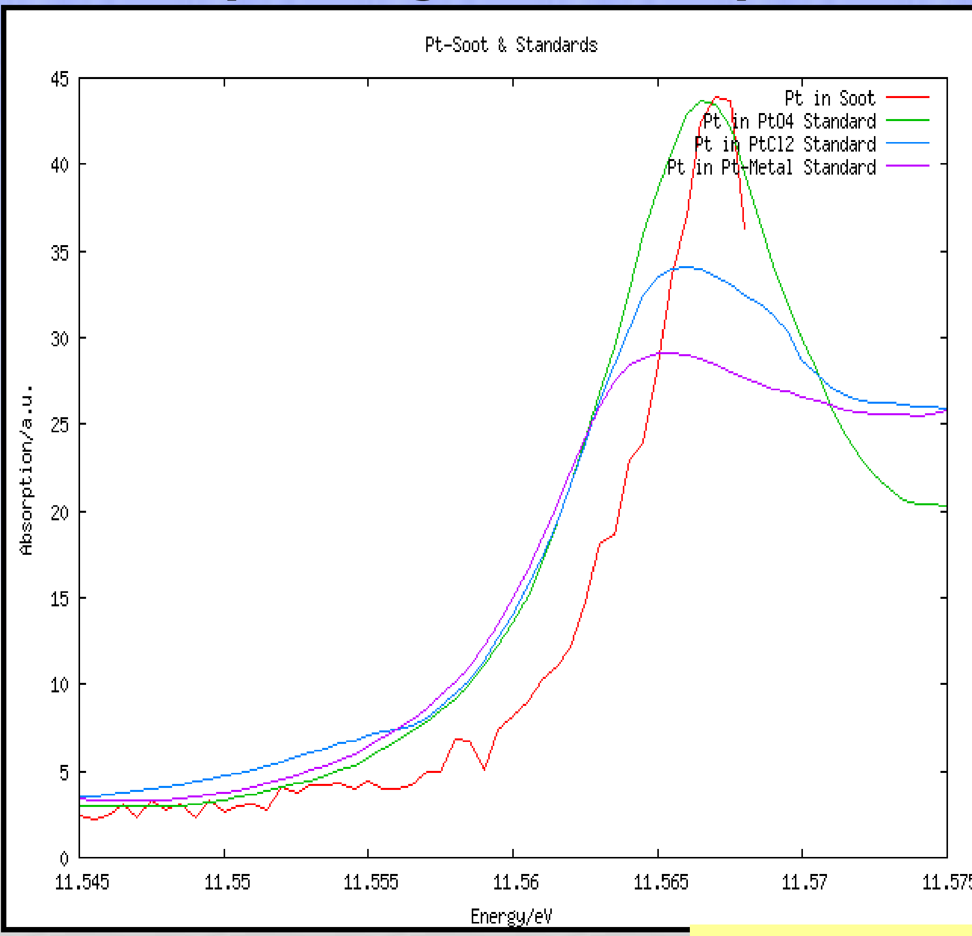
Spot #	Elemental Composition	Linear Least-Squares Fit Results
0	Ce, Zn, S	88% Pt-alumina, 7% Pt-foil, 5% **TCP**
1	Ce	56% Pt-alumina, 21% Pt-C, 24% PtO_2
2	Fe-rich	87% Pt-alumina, 10% PtO2, 3% HCP
3	Pt alone	81% Pt-alumina, 18% PtO2, 2% TCP
4	Ca, S	59% Pt-foil, 41% PtO_2
5	S-rich	86% Pt-C, 11% TCP, 7% Pt-alumina
6	Ce	86% Pt-alumina, 14% PtO_2, 3% HCP
7	Pt-rich	100% Pt-foil
8	Ce, Pt-rich	64% Pt-alumina, 11% PtO_2, 26% Pt-foil
9	Ce-rich	36% Pt-foil, 7% HCP, 59% Pt-C

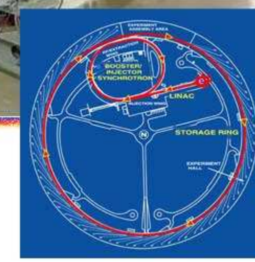
Large heterogeneities in particle composition are observed with many particles exhibiting a significant oxidized platinum component.

Strong evidence for PtO_2 (14-25% in many spots, up to 40% when associated with Ca and S), and less compelling evidence for presence of chloroplatinates.

Platinum bulk-XANES

XAS Spectra of Platinum Standards and Diesel Engine Exhaust PM (Running Pt-FBC Fuel)





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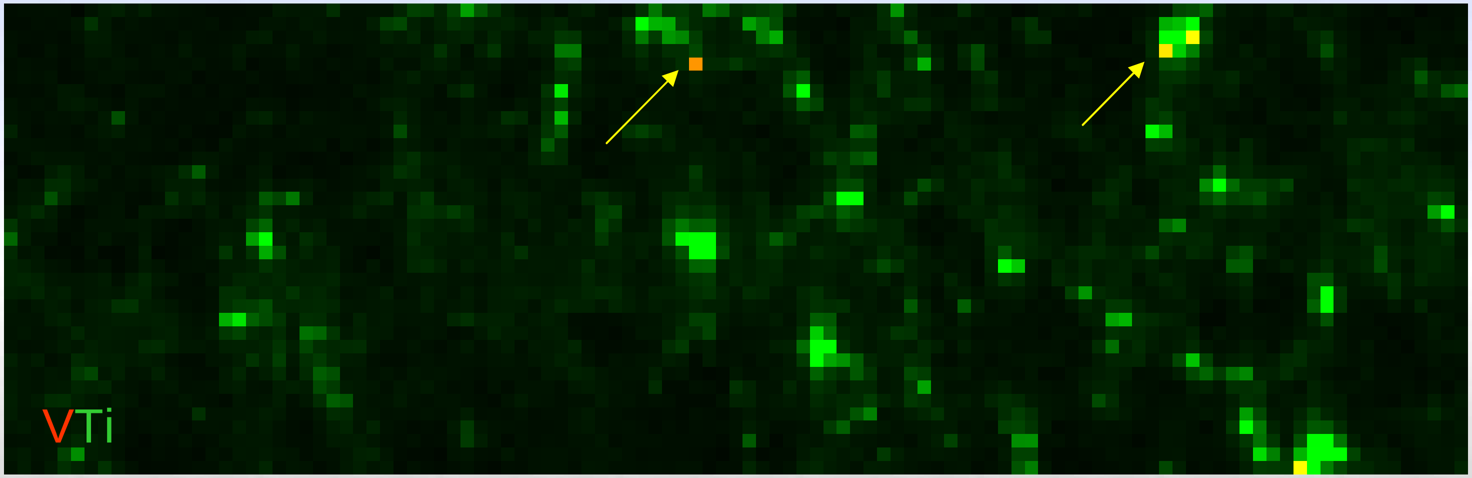
Shafer, M.M., J.J. Schauer, W. Copan, J. Peter-Hoblyn, B. Sprague, and J. Valentine. 2007. Investigation of platinum and cerium from use of a fuel-based catalyst. *SAE 2006 Transactions Journal of Fuels and Lubricants* – 2006-1-1517:491-503.

XRF Maps of Diesel Exhaust Particulates Impacted on Teflon PCIS Subsrates (engine running with a vanadium SCR)



Strong evidence of V, Ti –rich particles in engine PM

Preliminary e-XANES suggests V(V)

Acknowledgments

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BERKELEY LAB

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

HEI

Argonne
NATIONAL LABORATORY

Comparison of Water & Solvent – Speciated Platinum Emissions

- ❑Significantly more Pt extracted with MeOH (28 ± 1.4%) than with DCM (0.79 ± 0.15%) or water.
- ❑DCM should not extract ionic Pt species (except via physical process).
- ❑DCM more selective in isolating any Pt associated with organic matter.
- ❑Methanol (MeOH) extracts and disperses both polar and non-polar species. Breaks up diesel PM soot matrix. High MeOH extractables fraction does not indicate the presence of a large pool of organo-Pt species.